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Density fitting and Cholesky decomposition approximations in symmetry-adapted perturbation theory: Implementation and application to probe the nature of π-π interactions in linear acenes

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Density fitting (DF) approximations have been used to increase the efficiency of several quantum mechanical methods. In this work, we apply DF and a related approach, Cholesky decomposition (CD), to wave function-based symmetry-adapted perturbation theory (SAPT). We also test the one-center approximation to the Cholesky decomposition. The DF and CD approximations lead to a dramatic improvement in the overall computational cost of SAPT, while introducing negligible errors. For typical target accuracies, the Cholesky basis needed is noticeably smaller than the DF basis (although the cost of constructing the Cholesky vectors is slightly greater than that of constructing the three-index DF integrals). The SAPT program developed in this work is applied to the interactions between acenes previously studied by Grimme [Angew. Chem., Int. Ed. **47**, 3430 (2008)], expanding the cases studied by adding the pentacene dimer. The SAPT decomposition of the acene interactions provides a more realistic picture of the interactions than that from the energy decomposition analysis previously reported. The data suggest that parallel-displaced and T-shaped acene dimers both feature a special stabilizing π-π interaction arising from electron correlation terms which are significantly more stabilizing than expected on the basis of pairwise $-C_6R^{-6}$ estimates. These terms are qualitatively the same in T-shaped as in parallel-displaced geometries, although they are roughly a factor of 2 smaller in T-shaped geometries because of the larger distances between the intermolecular pairs of electrons. © *2010 American Institute of Physics*. [doi:10.1063/1.3426316]

I. INTRODUCTION

The ability to accurately and efficiently describe noncovalent interactions is crucial for the study of a wide variety of chemical systems. Considerable effort has been spent examining the hydrogen bonding and stacking of nucleic acid base pairs in DNA,[1–6] the interactions between the side chains of amino acids that influence the structure of proteins,[7–11] drug binding,[12] the structure and lattice energy of organic crystals,[13–16] and intercalation phenomena.[2,17–19] To explore these interactions, computational approaches ranging from highly correlated electronic structure methods to empirical approaches using molecular mechanics force fields are employed. There is, of course, an inherent tradeoff between the size of systems which can be examined and the accuracy of the computations. Coupled-cluster with singles and doubles including perturbative triples [CCSD(T)] (Ref. 20) is currently the benchmark method for noncovalent interactions because of its ability to capture electron correlation effects at all relevant length scales.[21–23] Due to the formal $O(N^7)$ complexity of this method, it is only applicable for small model systems (although recent work in local correlation techniques aims to extend the reach of coupled-cluster methods to larger molecules).[24–27] Besides the computational cost of the method, another drawback of the highly accurate CCSD(T) method is that it only provides a total interaction energy. In many cases, however, a decomposition of this energy is necessary to understand the fundamental behavior of an interaction. There are various energy decomposition techniques available,[28–33] but perhaps the most well-defined and robust is the symmetry-adapted perturbation theory (SAPT).[33]

The wave function-based formulation of SAPT has been shown to accurately reproduce benchmark potential energy curves for small, gas-phase dimers. A review by Jeziorski *et al.* describes the development and applications of wave function-based SAPT.[33] Unfortunately, there is a significant computational expense associated with the description of intramonomer electron correlation in SAPT. In order to treat extended systems, there are two approaches available. Neglecting intramonomer electron correlation in the wave function based formalism yields zeroth-order SAPT (denoted SAPT0, although note that at least second-order terms in the intermolecular potential are retained). Alternatively, density functional theory (DFT) based SAPT [SAPT(DFT)] is similar to SAPT0, but intramonomer electron correlation is accounted for by the density functional used.[34–38]

In addition to these approximations to the theory, one may also employ general numerical approximation schemes which apply to many different electronic structure methods.

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In particular, the use of approximate representations of two-electron integrals has become popular as a means to speed up their evaluation and reduce storage requirements. There are several closely related approaches to approximate two-electron integrals. The two discussed in this work are the density fitting (DF) approximation (DF, also called resolution-of-the-identity or RI)[39–46] and the Cholesky decomposition (CD).[47–50] In practice, both methods approximate the two-electron, four-index quantities as a linear combination of three-index quantities. The DF approach utilizes three-index integrals where one-index corresponds to a pre-optimized auxiliary basis set of atom-centered Gaussians [the auxiliary basis is typically a few times larger than the size of the chosen atomic orbital (AO) basis set]. This is very similar to the pseudospectral approximation,[51,52] which evaluates the third index on a grid. The CD approach guarantees the AO integrals to a certain accuracy, and is independent of particular electronic structure method. It has a slightly larger overhead associated with the computation of AO three-index quantities as compared to DF, but the result is an unbiased, method-independent approximation of the two-electron integrals. A general comparison of DF and CD methods has recently been published by Weigend *et al.*[53]

The DF approximation has been applied to SAPT in the context of SAPT(DFT).[54–56] This approximation reduces the bottleneck associated with the evaluation of the dispersion term from the SAPT(DFT) computation and allows the method to be applicable to larger systems. SAPT(DFT) computations have been performed on the benzene dimer using an aug-cc-pVQZ basis set, which includes more than 1500 basis functions.[55] One of the largest systems studied with the SAPT(DFT) method is the $2(H_2)-C_{60}$ complex with a TZ-VPP basis set by Korona *et al.*[57] There are several considerations for SAPT(DFT) computations that are not necessary in wave function based SAPT. To produce reasonable interaction energies, SAPT(DFT) requires an asymptotic correction. One of the more widely used corrections requires the ionization potentials of the monomers. The evaluation of the dispersion interaction in SAPT(DFT) scales as $\mathcal{O}(n^6)$, and DF can reduce this to $\mathcal{O}(n^4)$ for pure density functionals, and to $\mathcal{O}(n^5)$ with hybrid functionals [including Hartree–Fock (HF) exchange]. The hybrid functionals are usually more accurate,[54] but the available implementations of DF-SAPT(DFT) do not include exact (HF) exchange when the dispersion term is evaluated.[58,59] To circumvent this problem, the dispersion energy can be evaluated with a local density approximation (LDA) kernel; this introduces less than 1% deviation from the dispersion evaluated with generalized gradient approximation (GGA) kernels.[38,56] This approximation recovers the accuracy of the hybrid functionals, through the use of the hybrid GGA orbitals, while still scaling $\mathcal{O}(n^4)$. Finally, the inclusion of induced-multipole induced-multipole interactions in SAPT is not done explicitly, but rather by computing a δHF term. This term is computed as the difference between the SAPT0 energy (excluding dispersion) and the HF interaction energy. This cannot be computed from SAPT(DFT), and if it is needed, a separate wave function-based SAPT0 computation is required.

In this work we apply the DF and CD approximations to SAPT0. The performance of each method is assessed for individual molecular integrals as well as the various SAPT terms. To the best of our knowledge, this is the first study that focuses on DF in the context of wave function-based SAPT. Also, this is the first report of any type of Cholesky-based SAPT. We show that for large systems, the CD approach requires a smaller "fitting basis" to achieve comparable accuracy to the DF approach. The computer program whose development is reported here will be released in an upcoming version of the open-source electronic structure package, PSI.[60]

To assess the performance of DF and CD-SAPT0, dimers from the S22 test set of Hobza and co-workers were used.[6] Our DF-SAPT code was also applied to parallel-displaced and T-shaped linear acenes. Because of the efficiency of our DF integrals, we were able to study systems as large as the saturated analog of the pentacene dimer (116 atoms). Previous work using SAPT(DFT) to study acene interactions only treated systems up to as pyrene dimer (52 atoms).[61] Another study on linear acenes by Grimme,[62] which used a simpler Morokuma-type energy decomposition analysis,[28,29] stopped at tetracene dimer (60 atoms). A more recent work by Podeszwa studied the interaction between coronene dimers (72 atoms), which stands as the largest previous SAPT computation in terms of the number of atoms.[63]

II. THEORETICAL METHODS

SAPT provides a means of directly computing noncovalent interactions between molecules. A zeroth-order Hamiltonian is defined as the sum of monomer Hamiltonians, $H_0 = H_A + H_B$, where $H_A = F_A + W_A$. Here F_A is the Fock operator for monomer A, and W_A accounts for the intramolecular electron correlation of monomer A. An intermolecular operator, V, is defined as the difference between H_0 and the full dimer Hamiltonian, $V = H - H_0$. The full dimer Hamiltonian is given by

$$H = F_A + F_B + W_A + W_B + V. \tag{1}$$

In this work, we will focus on the leading SAPT terms, which are zeroth order in W. This truncation of SAPT is denoted SAPT0; it roughly captures all of the intermolecular terms in HF theory and the dispersion components of second-order Møller–Plesset perturbation theory (MP2). The quality of intermolecular interaction energies is thus similar for SAPT0 and supermolecular MP2, especially for dispersion-dominated complexes. SAPT has the added advantage of being free from basis set superposition error. The SAPT0 interaction energy is defined by

$$E_{\mathrm{SAPT0}} = E_{\mathrm{elst}}^{(10)} + E_{\mathrm{exch}}^{(10)} + E_{\mathrm{ind,resp}}^{(20)} + E_{\mathrm{exch\text{-}ind,resp}}^{(20)} + E_{\mathrm{disp}}^{(20)} + E_{\mathrm{exch\text{-}disp}}^{(20)}, \tag{2}$$

where the individual terms are defined in Ref. 64; the first number in parentheses denotes the perturbation order in V, and the second number in parentheses denotes the perturbation order in W. We refer the reader to Ref. 33 for a discussion on the accuracy of SAPT; SAPT0 interaction energies will typically be within 20%–30% of benchmark values.

The two-electron integrals in the DF approximation are given by

$$(\mu\nu|\rho\sigma) \approx \sum_{PQ} (\mu\nu|P)[J^{-1}]_{PQ}(Q|\rho\sigma). \tag{3}$$

The two-index quantity, $[J^{-1}]_{PQ}$, is the inverse of the Coulomb metric evaluated in an auxiliary basis set

$$[J]_{PQ} = \int P(\mathbf{r}_1)\frac{1}{r_{12}}Q(\mathbf{r}_2)d^3\mathbf{r}_1 d^3\mathbf{r}_2. \tag{4}$$

Ignoring any sparsity due to large distances between centers, there are $\mathcal{O}(N_{\mathrm{DF}}N_{\mathrm{AO}}^2)$ three-index integrals in the DF approach, compared to $\mathcal{O}(N_{\mathrm{AO}}^4)$ two-electron integrals. It is convenient to rewrite Eq. (3) with different three-index quantities,

$$\widetilde{(\mu\nu|Q)} = \sum_{P} (\mu\nu|P)[J^{-1/2}]_{PQ}, \tag{5}$$

$$(\mu\nu|\rho\sigma) \approx \sum_{Q} \widetilde{(\mu\nu|Q)}\widetilde{(Q|\rho\sigma)}. \tag{6}$$

In SAPT, the three-index terms must be transformed into the molecular orbital (MO) basis of each monomer,

$$\widetilde{(ij|Q)} = \sum_{\mu\nu} C_{\mu i}^{M\dagger}\widetilde{(\mu\nu|Q)}C_{\nu j}^{N}, \tag{7}$$

where C^M and C^N represent the SCF coefficient matrices of monomers M and N, and where i and j are MOs resulting from the HF computations on monomers M and N, respectively. All the two-electron integrals necessary in SAPT can be formed from the $\widetilde{(ij|Q)}$ quantities through the MO basis analog of Eq. (6).

The intermediate quantities that result from a CD, $L_{\mu\nu}^{Q}$, are analogous to the $\widetilde{(\mu\nu|Q)}$ three center integrals

$$(\mu\nu|\rho\sigma) \approx \sum_{Q} L_{\mu\nu}^{Q}L_{\rho\sigma}^{Q}. \tag{8}$$

The Cholesky vectors are defined recursively through

$$L_{\rho\sigma}^{\rho\sigma} = \sqrt{(\rho\sigma|\rho\sigma) - \sum_{n=0}^{\rho\sigma_{\max}-1} L_{\rho\sigma}^{n}L_{\rho\sigma}^{n}}, \tag{9}$$

$$L_{\mu\nu}^{\rho\sigma} = \frac{1}{L_{\rho\sigma}^{\rho\sigma}}\left((\mu\nu|\rho\sigma) - \sum_{n=0}^{\rho\sigma_{\max}-1} L_{\mu\nu}^{n}L_{\rho\sigma}^{n}\right), \quad \mu\nu \neq \rho\sigma. \tag{10}$$

The Cholesky vectors can be transformed for SAPT using an analog of Eq. (7).

$$L_{ij}^{Q} = \sum_{\mu\nu} C_{\mu i}^{M\dagger}L_{\mu\nu}^{Q}C_{\nu j}^{N}. \tag{11}$$

The AO two-electron integrals can be approximated to an accuracy of δ using the Cholesky procedure. If the $(\rho\sigma|\rho\sigma)$ integrals are ordered from largest to smallest, only the Cholesky vectors where $L_{\rho\sigma}^{\rho\sigma}L_{\rho\sigma}^{\rho\sigma} > \delta$ need to be formed. A further approximation can be made to the CD by including only $\rho\sigma$ pairs where ρ and σ are centered on the same nucleus. This is referred to as a one-center CD (1C-CD).[65,66] Although formally it removes the error bound on the approximate integrals, in practice, the error made in the one-center approximation is minimal.

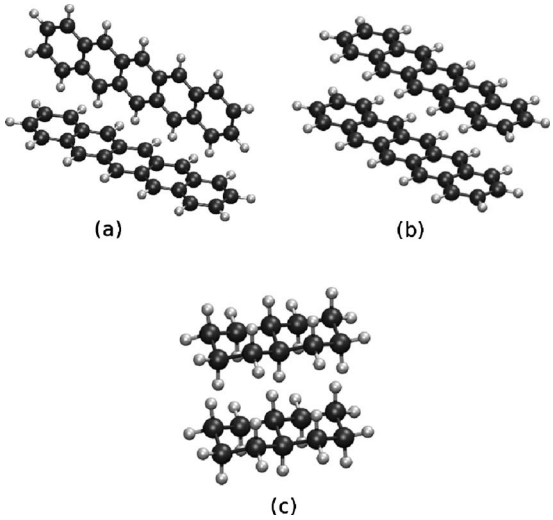

FIG. 1. Geometries of (a) T-shaped, (b) parallel-displaced pentacene dimer and (c) the saturated analouge of naphthalene dimer. The centers of the rings in the T-shaped dimers are separated by 5.0 Å. The parallel-displaced geometries are separated by 3.5 Å vertically and 1.7 Å horizontally. These intermolecular distances are those which are optimal for the benzene dimer (Ref. 23). The carbon atoms in the saturated dimers are all separated by approximately 4.3 Å (Ref. 62).

In addition to the DF and CD type approximations, the Cauchy–Schwartz inequality can be applied to avoid computing unnecessary integrals. A conservative screening threshold of 10^{-12} E_h on the two-electron integrals used to perform the CD as well as the three-index AO DF integrals was determined *a posteriori* from SAPT0 computations on small, weakly bound dimers and applied to all SAPT computations throughout this work.

Molecular geometries used here are taken from the S22 test set of Hobza and co-workers.[6] Computations are performed with the Dunning aug-cc-pVXZ basis sets.[67,68] The complimentary aug-cc-pVXZ-RI basis sets[69] are employed in the DF-SAPT computations. All SAPT computations were performed with a modified version of PSI 3.4.[60] In this implementation of SAPT, the terms are always evaluated in the dimer basis, although the equations we have implemented are valid in the monomer basis as well.

Our newly developed DF-SAPT program has been applied to study the differences between parallel-displaced and T-shaped configurations of linear acenes, as shown in Fig. 1. We will consider the $n=1$ (benzene dimer) through $n=5$ (pentacene dimer) cases. In order to isolate the changes in the interaction due to the additional rings, the CC and CH bond distances are held at their lengths in benzene, 1.3915 and 1.080 Å, respectively.[70] Additionally, the intermolecular displacements are fixed at the values that are optimal for the benzene dimer.[23] For comparison purposes, we also considered saturated, stacked dimers beginning with the cyclohexane dimer, using the geometry of Grimme.[62] Larger saturated dimers were constructed from the cyclohexane dimer without reoptimization of geometrical coordinates (consistent with our method of constructing the aromatic dimer geometries). These constraints greatly simplify the energy component

TABLE I. Deviation (in microhartree) from conventional SAPT0/aug-cc-pVDZ for water dimer, ammonia dimer, and methane dimer. [The geometries are taken from the S22 test set (Ref. 6).]

	DF-SAPT	CD-SAPT		1C-CD-SAPT	
		10^{-3}	10^{-4}	10^{-3}	10^{-4}
		Water dimer			
N[a]	236	221	389	213	316
$E_{\text{elst}}^{(10)}$	1.52	−2.16	0.04	0.08	0.08
$E_{\text{exch}}^{(10)}$	4.63	6.43	0.55	5.10	0.69
$E_{\text{ind,resp}}^{(20)}$	1.28	−0.03	0.05	−0.71	0.05
$E_{\text{exch-ind,resp}}^{(20)}$	−0.24	−0.04	−0.01	0.09	0.01
$E_{\text{disp}}^{(20)}$	0.49	−0.25	−0.09	−1.35	−0.04
$E_{\text{exch-disp}}^{(20)}$	−1.76	−2.75	−0.13	−0.95	−0.22
E_{SAPT0}	5.93	1.20	0.41	2.25	0.57
		Ammonia dimer			
N[a]	282	247	412	244	355
$E_{\text{elst}}^{(10)}$	−1.07	−0.86	−0.12	−1.24	0.09
$E_{\text{exch}}^{(10)}$	5.15	8.37	1.13	7.14	2.11
$E_{\text{ind,resp}}^{(20)}$	0.03	−0.05	0.00	0.31	−0.10
$E_{\text{exch-ind,resp}}^{(20)}$	−0.03	0.00	−0.02	−0.29	−0.01
$E_{\text{disp}}^{(20)}$	−0.35	−0.19	−0.12	−1.66	0.04
$E_{\text{exch-disp}}^{(20)}$	−1.24	−2.58	−0.27	−1.78	−0.55
E_{SAPT0}	2.50	4.69	0.59	2.46	1.58
		Methane dimer			
N[a]	328	278	450	260	392
$E_{\text{elst}}^{(10)}$	−4.35	−0.06	−0.01	0.07	−0.10
$E_{\text{exch}}^{(10)}$	2.53	2.70	0.64	2.81	0.67
$E_{\text{ind,resp}}^{(20)}$	−0.02	0.01	0.00	0.01	0.00
$E_{\text{exch-ind,resp}}^{(20)}$	0.01	−0.01	0.00	−0.01	0.00
$E_{\text{disp}}^{(20)}$	−0.38	−0.25	0.01	−0.47	−0.06
$E_{\text{exch-disp}}^{(20)}$	−0.68	−1.13	−0.29	−0.97	−0.27
E_{SAPT0}	−2.90	1.27	0.34	1.43	0.24

[a]Number of functions in the DF or CD basis.

analysis because some of the terms are very sensitive to geometry and therefore difficult to compare in dimers with different intermolecular distances. The SAPT0 computations on the acene dimers were performed with a truncated aug-cc-pVDZ basis set denoted aug-cc-pVDZ′. This basis set removes all diffuse functions from hydrogen atoms and diffuse *d* functions from carbon atoms. In our experience, fortuitous error cancellation occurs for aromatic dimers when this basis set is paired with MP2-like methods.[21] This basis is somewhat smaller than needed for accurate interaction energies of the saturated dimers (see below), but it should suffice for a semiquantitative analysis of the energy components. A truncated aug-cc-pVDZ-RI fitting basis set was paired with the aug-cc-pVDZ′ orbital basis: the diffuse functions were removed from the fitting basis for hydrogen atoms and diffuse *f* functions were removed for carbon atoms.

III. RESULTS AND DISCUSSION

A. Performance

The approximate SAPT0 methods were assessed on the basis of their ability to reproduce the necessary MO integrals and on the deviation of the SAPT0 components. In this work, we will utilize the naming convention for MO indices common in the SAPT literature. The occupied and virtual orbitals of monomer A will be labeled *a* and *r*, respectively. The occupied and virtual orbitals of monomer B will be labeled *b* and *s*, respectively. It is important to note that the CD guarantees the AO integrals to a specified accuracy; however, this error bound does not apply to the transformed MO integrals. For the purpose of computing SAPT0 energies, it was found that a CD threshold of 10^{-3}–10^{-4} E_h was reasonable. For a given AO basis, the former value tends to create a slightly smaller Cholesky basis than the corresponding DF basis, while the latter value will create a significantly larger Cholesky basis. This is illustrated in Table I, which compares fitting basis size and errors in the SAPT0 energy components for the water, ammonia, and methane dimers.

Through a comparison of the approximate DF and CD MO integrals with the exact integrals, it was determined that the largest errors occur for the integrals centered entirely on one monomer in both cases. This includes the *aarr*, *arar*, *bbss*, and *bsbs* classes of integrals. Because these integrals are greater in magnitude than those which span both monomers, this result is not surprising. The largest errors for these integrals tend to be on the order of 10^{-1} E_h. In SAPT0, these integrals are used only to compute the orbital response coefficients that are involved in the evaluation of the $E_{\text{ind,resp}}^{(20)}$ and

TABLE II. Errors (in kcal mol^{-1}) of DF-SAPT and 1C-CD-SAPT for the S22 test set (Ref. 6) relative to conventional SAPT0/aug-cc-pVDZ.

	MAX[a]	MSE[b]	MUE[c]	RMS[d]
		DF-SAPT		
$E_{\text{elst}}^{(10)}$	0.003	0.000	0.001	0.001
$E_{\text{exch}}^{(10)}$	0.014	0.005	0.005	0.007
$E_{\text{ind,resp}}^{(20)}$	0.002	0.000	0.000	0.001
$E_{\text{exch-ind,resp}}^{(20)}$	0.000	0.000	0.000	0.000
$E_{\text{disp}}^{(20)}$	0.002	0.000	0.001	0.001
$E_{\text{exch-disp}}^{(20)}$	0.007	−0.003	0.003	0.003
E_{SAPT0}	0.006	0.002	0.003	0.003
		1C-CD-SAPT[e]		
$E_{\text{elst}}^{(10)}$	0.006	0.000	0.001	0.002
$E_{\text{exch}}^{(10)}$	0.057	0.011	0.011	0.017
$E_{\text{ind,resp}}^{(20)}$	0.006	−0.001	0.001	0.002
$E_{\text{exch-ind,resp}}^{(20)}$	0.002	0.000	0.000	0.001
$E_{\text{disp}}^{(20)}$	0.003	−0.001	0.001	0.001
$E_{\text{exch-disp}}^{(20)}$	0.038	−0.007	0.007	0.011
E_{SAPT0}	0.023	0.002	0.003	0.006

[a]Maximum absolute error.
[b]Mean signed error.
[c]Mean unsigned error.
[d]Root mean square error.
[e]AO integrals computed with a tolerance of 10^{-3} E_h.

$E_{\text{exch-ind,resp}}^{(20)}$ terms. These integrals do not directly contribute to the SAPT0 energy, but they affect the energy indirectly when the response coefficients are contracted against the *arbb* or *aabs* type integrals. As shown in Tables I and II, the error incurred in the evaluation of the $E_{\text{ind,resp}}^{(20)}$ and $E_{\text{exch-ind,resp}}^{(20)}$ terms with approximate integrals is negligible.

As indicated in Table I, the 1C-CD-SAPT results are very similar to those for CD-SAPT and for low tolerances, the size of the Cholesky basis is not reduced significantly. However, the automatic exclusion of two-center terms from the Cholesky basis makes the 1C-CD algorithm more efficient than the full CD algorithm. It is apparent that for the three small test systems in Table I, a CD tolerance of 10^{-3} is acceptable for obtaining very accurate SAPT0 energy components, with errors of less than 0.01 millihartree (0.006 kcal mol^{-1}). Of the CD methods shown in Table I, the 1C-CD-SAPT with a tolerance of 10^{-3} appears to have the most promise for general applicability.

At this point, it should be noted that, in practice, the error associated with the three-index integral approximations for the SAPT0 total interaction energy may only depend on the $E_{\text{disp}}^{(20)}$ and $E_{\text{exch-disp}}^{(20)}$ terms (assuming the integral approximations are not also used for the HF computations). Often, a $\delta E_{\text{ind,resp}}^{(\text{HF})}$ term is computed from the HF interaction energy as

$$\delta E_{\text{ind,resp}}^{(\text{HF})} = E_{\text{int}}^{\text{HF}} - (E_{\text{elst}}^{(10)} + E_{\text{exch}}^{(10)} + E_{\text{ind,resp}}^{(20)} + E_{\text{exch-ind,resp}}^{(20)}). \tag{12}$$

This term captures induced-multipole induced-multipole interactions that are not described by the $E_{\text{ind,resp}}^{(20)}$ and $E_{\text{exch-ind,resp}}^{(20)}$ terms. In CD- or DF-SAPT0, adding this term also has the effect of removing some fitting error from the total SAPT0 energy, since our SAPT implementation uses exact HF computations as a starting point. It is also important to note that SAPT computations are generally used to get a qualitative understanding of the fundamental physics of nonbonded interactions. A deviation of a few hundredths of one kcal mol^{-1} does not affect the SAPT results qualitatively. It should also be noted that SAPT is a perturbational method of computing interaction energies directly; as a consequence, the fitting error that occurs with SAPT is much smaller than the fitting error that occurs in an MP2 total energy, for example. This is somewhat similar to the observation by Böstrom *et al.*[71,72] that the CD threshold does not need to be as tight for excitation energy computations as it is for total energy computations.

To assess the performance of the 1C-CD-SAPT0 with a tolerance of 10^{-3}, this method and DF-SAPT0 were applied to the S22 test set. These results are shown in Table II. As mentioned previously, the errors for the induction terms are negligible; for these cases, the error is always less than a hundredth of a kcal mol^{-1}. Perhaps surprisingly, the error in the electrostatic term is also very low. This term contains a small number of fairly large two-electron integrals; evidently, the *aabb* type integrals are approximated well by both methods. The largest errors occur in the evaluation of the exchange term; a large number of *oooo* type integrals (all occupied orbitals) are involved in the evaluation of this term. It is possible (and seems likely) that systematic errors accumulate during the evaluation of this term. The accuracy of the 1C-CD-SAPT0 with the chosen tolerance is not quite as good as that of DF-SAPT0, but the errors incurred by 1C-CD-SAPT0 are acceptable given the smaller CD basis.

The number of basis functions needed for each complex in the S22 test set is shown in Table III. For the larger complexes in the set, a CD basis needs to be only about 75%–80% of the DF basis size. Once the three-index AO quantities (DF three-index integrals or CD vectors, which we will refer to generically as three-index integrals) have been computed, the first step of the transformation to the MO basis scales as $\mathcal{O}(N_{\text{AUX}}N_{\text{AO}}^2N_{\text{MO}})$. By reducing the size of the auxiliary basis, the expense of this step as well as the storage requirements for the three-index integrals is reduced. The next step is the formation of the four-index MO integrals from the transformed three-index integrals. Assuming that all the MO integrals are needed (and ignoring any sparsity), this step scales as $\mathcal{O}(N_{\text{AUX}}N_{\text{MO}}^4)$. The most computational savings from a smaller fitting basis is possible in this step. Due to the fact that the formation of the Cholesky basis is slightly more intensive than the formation of the DF integrals, to be competitive with DF the Cholesky basis needs to be smaller than a DF basis that performs with comparable accuracy. As systems become larger, the work associated with the formation of the three-index CD or DF integrals becomes negligible compared to the rest of the computation. At some point, the formation of the MO four-index integrals from the three-index integrals should become much more time consuming, and beyond this point 1C-CD-SAPT may become significantly more efficient than DF-SAPT.

B. Timings

We have performed timings of our SAPT program to understand the practical aspects of the DF and CD approxi-

TABLE III. Number of auxiliary basis functions required for each complex in the S22 test set. (Computations performed with the aug-cc-pVDZ basis.)

	DF-SAPT[a]	1C-CD-SAPT[b]
H-bonded complexes		
$(NH_3)_2$	282	244
$(H_2O)_2$	236	213
Formic acid dimer	524	465
Formamide dimer	570	488
Uracil dimer	1336	1073
2-pyridoxine·2-aminopyridine	1261	970
Adenine·thymine WC	1621	1270
Dispersion dominated complexes		
$(CH_4)_2$	328	260
$(C_2H_4)_2$	472	375
Benzene·CH_4	734	549
PD benzene dimer	1140	848
Pyrazine dimer	1048	810
Uracil dimer	1336	1080
Stacked Indole·benzene	1379	1016
Stacked Adenine·thymine	1621	1265
Mixed complexes		
Ethene·ethine	426	349
Benzene·H_2O	688	540
Benzene·NH_3	711	545
Benzene·HCN	737	572
T-shaped benzene dimer	1140	847
T-shaped indole benzene	1379	1030
Phenol dimer	1284	978

[a]The aug-cc-pVDZ-RI basis was used.
[b]AO integrals computed with a tolerance of 10^{-3} E_h.

mations in SAPT0. All the computations reported in this section were run on a quad-core Intel Xeon E5430 processor clocked at 2.66 GHz. We also compared the timings of our conventional integral transformation to the SAPT2008 program.[58] Both programs perform very similarly, so we will only show timings from our SAPT program.

DF- and CD-SAPT0 energies were computed for formic acid dimer, methane-benzene, T-shaped benzene dimer, T-shaped indole-benzene, and hydrogen bonded adenine-thymine. All of these complexes are taken from the S22 test set, and energies were computed with an aug-cc-pVDZ basis. The timings of the computation of the integrals required for the SAPT0 evaluation are shown in Fig. 2. The "MO three-index" timing refers to the formation of AO three-index integrals (i.e., $(\widetilde{\mu\nu|Q})$ or $L^Q_{\mu\nu}$ quantities) and their transformation to the MO basis. The "MO four-index" timing refers to the formation of the approximate four-index MO integrals from the three-index MO integrals. Performing a CD is more expensive than DF in the formation of AO three-index quantities, but the reduction in size of the fitting basis recovers the overhead of the CD in the subsequent steps. The overall time for integral processing is nearly identical for the DF and CD approaches, with the CD approach becoming slightly more efficient beyond about 450 orbitals. Both CD and DF are much more efficient than the conventional integral transformation.

The tolerance chosen for the CD led to slightly larger

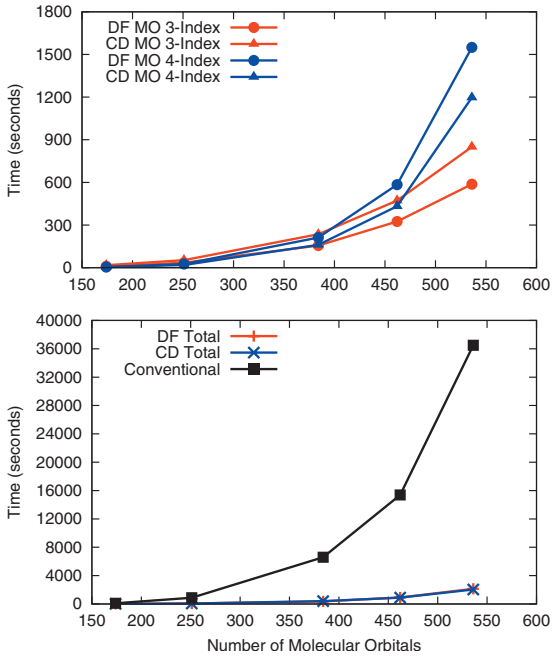

FIG. 2. Timings of DF, CD, and conventional integral evaluation for SAPT0 computations on selected complexes from the S22 test set (Ref. 6) with an aug-cc-pVDZ basis. "Four-index" timings refer to the construction of the four-index integrals from the three-index integrals.

errors in the SAPT energy components than in the DF approach; however, the errors remain no larger than a few hundredths of 1 kcal mol^{-1} (see Table II). However, with the desire to study much larger systems and higher order corrections to the SAPT energy (which require additional groups of integrals such as the expensive *vvvv* type) the CD-SAPT approach could become significantly more efficient than DF-SAPT.

Figure 3 shows the timings for the DF-SAPT0 computations performed on the T-shaped acene dimers. As the size of the DF-SAPT0 computations approaches 1000 MOs, formation of the four-index MO integrals dominates; the scaling of this step is $\mathcal{O}(N_{\mathrm{AUX}}o^2v^2)$. This step is far more costly than the energy evaluation. The most expensive portion of the SAPT0 energy evaluation is the $E^{(20)}_{\mathrm{exch\text{-}disp}}$ term. This term conventionally scales as $\mathcal{O}(o^3v^2)$; Hesslemann and coworkers present equations in their SAPT(DFT) approach that

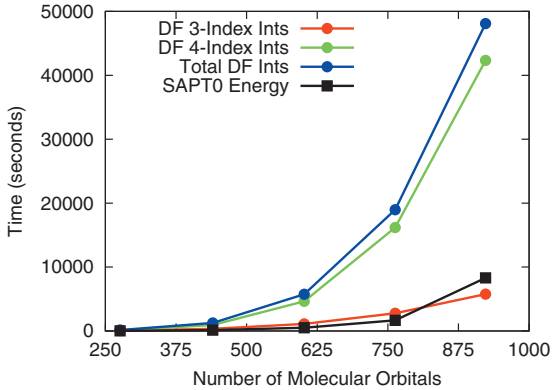

FIG. 3. Timings of DF-SAPT computations on T-shaped acene dimers with the aug-cc-pVDZ′ basis. Four-index timings refer to the construction of the four-index integrals from the three-index integrals.

use the DF representation of the two-electron integrals to evaluate the $E^{(20)}_{\text{exch-disp}}$ term in a manner that scales as $\mathcal{O}(N_{\text{AUX}}o^2v^2)$.[55] Such a formulation of the $E^{(20)}_{\text{exch-disp}}$ term is more memory efficient, but slightly more costly than the conventional implementation. By reducing the size of N_{AUX} relative to DF, such terms will be more efficient using the CD approach. Our implementation of the $E^{(20)}_{\text{exch-disp}}$ term uses the conventional algorithm for smaller systems and Hesselmann's approach for larger systems. The remaining terms in SAPT0 scale as $\mathcal{O}(o^2v^2)$ or better.

It is interesting to compare the scaling of SAPT0 to that of the supermolecular MP2 method. First, we will look at the scaling of SAPT0. As is evident from Figs. 2 and 3, the construction of the four-index MO integrals (whether by conventional transformation or by DF/CD approximations) is much more expensive than the energy evaluation [which scales as $\mathcal{O}(o^3v^2)$]. There are several types of four-index integrals required for SAPT0 that are potentially similar in size: the *aarr*, *bbss*, *arar*, *bsbs*, and *arbs* type integrals. It is possible to take advantage of the permutational symmetry of these integrals; the *arar* and *bsbs* type integrals have twofold symmetry and the *aarr* and *bbss* type integrals have fourfold symmetry. The *arbs* type integrals do not have any permutational symmetry, which makes them potentially the most expensive to compute. It is important to remember that for SAPT commutations, the occupied orbitals are divided into those from monomer A and those from monomer B. This makes a general comparison of the size of the various types of integrals impossible without knowing the relative sizes of the monomers. For simplicity, we will assume that the number of occupied orbitals on monomer A and monomer B are equal ($a=b$). Additionally we will assume that there are many more virtual orbitals than occupied orbital, since this is required for an accurate description of dispersion interactions ($a \ll r$ and $b \ll s$). With these assumptions, the asymptotic complexity of SAPT0 is $\mathcal{O}(aN^4_{AO})$ for conventional SAPT0 and $\mathcal{O}(arbsN_{\text{AUX}})$ for DF/CD SAPT0.

A counterpoise-corrected, supermolecular MP2 interaction energy requires three separate MP2 energy evaluations. The scaling of MP2 (much like SAPT0) is dominated by the formation of the four-index MO integrals. Each MP2 computation requires the construction of an o^2v^2 group of integrals and then and energy evaluation, which scales as only $\mathcal{O}(o^2v^2)$. For the monomer computations, MP2 requires *arar* and *bsbs* integrals (and recall that SAPT0 and counterpoise-corrected MP2 both use the full dimer basis to describe each monomer). These integrals have a twofold symmetry and are identical to those found in SAPT0. The dimer MP2 computation uses a larger occupied space than any of the stages in SAPT0. Here, $o=a+b$ and $v=N_{\text{MO}}-a-b$. With this definition of the occupied and virtual space, the integrals needed for the dimer MP2 computation are o^2v^2 in size. This is noticeably larger than any of the types of integrals in SAPT0 despite the twofold symmetry of these integrals. Therefore, the asymptotic complexity of an MP2 interaction energy computation is $\mathcal{O}(oN^4_{\text{AO}})$ for a conventional MP2 computation and $\mathcal{O}(ovovN_{\text{AUX}})$ for DF/CD-MP2. Thus, the scaling of a supermolecular (DF/CD-)MP2 interaction energy is worse than the scaling of (DF/CD-)SAPT0. In practice, however, each MO integral is only needed once to compute an MP2 energy, whereas each *ovov* integral is needed multiple times in SAPT0. For large systems, where the *ovov* arrays do not fit into memory, it is likely that it would be faster to compute an MP2 interaction energy than to compute an SAPT0 interaction energy, despite the scalings.

C. Application to acene dimers

The results for the SAPT0 decomposition of the acene dimers are given in Table IV. The total SAPT0 interaction energies for the acene dimers show good agreement with the SCS-MP2 and B97-D values reported by Grimme.[62] For the saturated stacked dimers, the dimers are somewhat underbound (by 27%–45%) compared to Grimme's MP2 results. We ascribe this difference to poorer error cancellation for the SAPT0/aug-cc-pVDZ′ level of theory for the saturated systems. Nevertheless, we believe the qualitative trends in the SAPT energy components will be reliable enough for our analysis; we will focus particularly on the dispersion energies, and our SAPT dispersion energies are quite similar to Grimme's B2PLYP-D/TZV(2d,p) dispersion energies.[62] For the purposes of this analysis,

$$E_{\text{ind}} = E^{(20)}_{\text{ind,resp}} + E^{(20)}_{\text{exch-ind,resp}} + \delta E^{(\text{HF})}_{\text{ind,resp}}, \tag{13}$$

and

$$E_{\text{disp}} = E^{(20)}_{\text{disp}} + E^{(20)}_{\text{exch-disp}}. \tag{14}$$

This grouping is somewhat arbitrary, since the $E^{(20)}_{\text{exch-ind,resp}}$ and $E^{(20)}_{\text{exch-disp}}$ terms are cross terms which explicitly include the effect of MO overlap.

For the acene dimers, the SAPT decomposition shows a linear increase in the E_{exch}, E_{elst}, and E_{ind} terms with the number of rings. The E_{disp} term shows a nonlinear increase that is consistent with the decomposition reported by Grimme.[62] Since the dispersion energy can be approximated as a pairwise $-C_6R^{-6}$ interaction, a nonlinear increase is expected. However, as shown in Table V, because of the finite range of the empirical dispersion correction, it increases only linearly past anthracene dimer, whereas the quantum mechanical SAPT0 dispersion energy shows nonlinearity in all the cases considered. It is important to note that this same behavior is seen in both the parallel-displaced and T-shaped dimers. The magnitude of the dispersion energy in the parallel-displaced dimers is obviously greater due to the closer interaction between π-clouds. These observations lead to the conclusion that the intrinsic dispersion interaction between π-electrons in both configurations is the same qualitatively. The difference in magnitude is simply a result of the separation between π-clouds.[73]

In Tables IV and V, the only geometric changes that occur are the addition of rings to the monomers. This isolates the electronic effects from geometric effects. Our analysis suggests that the nonlinear increase of the dispersion interaction seen in the aromatic complexes is purely an electronic effect that originates from the interaction of large, delocalized π-orbitals in relatively close proximity. In contrast to

TABLE IV. SAPT0 decomposition of the interactions within aromatic T-shaped and parallel-displaced acene dimers as well as the stacked, saturated dimers. (Computations performed with the aug-cc-pVDZ′ basis. Energies given in kcal mol^{-1}.)

N	E_{elst}	E_{exch}	E_{abab} [a]	E_{ind}	E_{disp}	$-C_6/R^6$ [b]	E_{SAPT0}
			Parallel-displaced, aromatic				
1	−1.62	6.08	−4.42	−0.67	−6.66	−4.73	−2.87
2	−2.95	9.65	−8.86	−0.90	−13.07	−8.97	−7.27
3	−4.31	13.15	−13.64	−1.13	−19.95	−13.32	−12.24
4	−5.69	16.60	−18.62	−1.38	−27.03	−17.69	−17.49
5	−7.07	20.01	−23.74	−1.66	−34.20	−22.06	−22.91
			T-shaped, aromatic				
1	−1.74	3.19	−2.35	−0.50	−3.73	−3.24	−2.78
2	−3.03	6.09	−5.47	−0.93	−7.95	−6.57	−5.81
3	−4.25	8.94	−9.06	−1.35	−12.48	−9.98	−9.13
4	−5.46	11.77	−12.93	−1.78	−17.13	−13.40	−12.60
5	−6.66	14.58	−16.98	−2.22	−21.84	−16.83	−16.15
			Stacked, saturated				
1	−2.72	8.75	−6.36	−0.84	−6.57	−7.56	−1.37
2	−5.24	16.46	−14.46	−1.56	−13.09	−14.32	−3.43
3	−7.75	24.17	−23.77	−2.28	−19.70	−21.20	−5.55
4	−10.26	31.89	−33.83	−2.99	−26.33	−28.10	−7.69
5	−12.77	39.60	−44.38	−3.71	−32.97	−35.01	−9.85

[a]Contribution to the exchange energy from *abab* type elements of the intermolecular potential.
[b]Atomic C_6 values taken from Ref. 75.

the aromatic dimers, the saturated dimers do not show a nonlinearity in the dispersion term beyond what is expected. Moreover, the changes in all of the energy components for the saturated complexes are more linear than in the aromatic complexes.

The $n=1$ to $n=4$ cases were previously studied by Grimme[62] in an attempt to determine if there is anything unique about π-π interactions. That work relies upon the results from a Morokuma style energy decomposition analysis (EDA).[28,29] The specifics of the EDA implementation used by Grimme are explained in Ref. 74. The EDA is benchmarked against SAPT and a discrepancy for the electrostatic and exchange terms is noted:[74] "Larger systematic differences between SAPT and EDA are observed for E_{exr} and E_{es}, i.e., the former is higher and latter is always lower in EDA. The reasons for this are presently not clear and deserve more research." When this approach is applied to acene dimers, the electrostatic term appears to be more attractive than the dispersion term by about a factor of two. This is curious since the interaction between nonpolar molecules is

TABLE V. Changes in energy components of aromatic and saturated interactions (in kcal mol^{-1}) as the number of rings are increased. (Computations performed with the aug-cc-pVDZ′ basis. Energy differences are computed as E_{N_2}-E_{N_1}.)

$N_1 \rightarrow N_2$	ΔE_{elst}	ΔE_{exch}	ΔE_{ind}	ΔE_{disp}	$\Delta(-C_6R^{-6})$	ΔE_{SAPT0}
			Parallel-displaced, aromatic			
$1 \rightarrow 2$	−1.33	3.57	−0.23	−6.41	−4.24	−4.40
$2 \rightarrow 3$	−1.37	3.50	−0.23	−6.88	−4.35	−4.97
$3 \rightarrow 4$	−1.38	3.45	−0.25	−7.08	−4.37	−5.25
$4 \rightarrow 5$	−1.38	3.41	−0.29	−7.17	−4.37	−5.42
			T-shaped, aromatic			
$1 \rightarrow 2$	−1.28	2.89	−0.43	−4.22	−3.33	−3.03
$2 \rightarrow 3$	−1.23	2.85	−0.42	−4.52	−3.41	−3.32
$3 \rightarrow 4$	−1.21	2.83	−0.43	−4.65	−3.43	−3.46
$4 \rightarrow 5$	−1.20	2.81	−0.44	−4.72	−3.43	−3.55
			Stacked, saturated			
$1 \rightarrow 2$	−2.52	7.71	−0.72	−6.53	−6.76	−2.06
$2 \rightarrow 3$	−2.51	7.71	−0.72	−6.60	−6.88	−2.11
$3 \rightarrow 4$	−2.51	7.72	−0.72	−6.63	−6.90	−2.15
$4 \rightarrow 5$	−2.51	7.72	−0.72	−6.64	−6.91	−2.15

expected to be dispersion-dominated. Due to this counterintuitive result, Grimme uses the sum of the exchange and electrostatic terms in his analysis.

In the implementation of EDA used by Grimme, the stabilizing *abab* type two-electron integrals that enter the HF energy expression are incorrectly included in the electrostatic term instead of the exchange term. In Table IV, we show the contribution from the *abab* interaction to the $E_{\mathrm{exch}}^{(10)}$ term separately. In the case of pentacene dimer, this stabilizing interaction is actually three times as large as the entire electrostatic term. By misplacing these contributions, the exchange and electrostatic results from Grimme's EDA appear much too large in magnitude and are difficult to reconcile physically. It should be noted that E_{abab}, reported here, is computed from complete elements of the intermolecular potential, whereas the terms misplaced in Grimme's EDA are only the two-electron contribution to E_{abab}. The EDA implementation reported in Ref. 74 could be fixed by separating the two-electron energy into coulomb and exchange contributions and adding each to the appropriate grouping. This issue is symptomatic of the specific implementation, not of the EDA outlined by Morokuma.

Because Grimme sums the exchange and electrostatic terms into a total first order interaction in his work on acene dimers, the problem with the EDA implementation did not affect the final conclusions of the paper, namely, that the increase in interaction energy with respect to system size is similar for T-shaped acenes and saturated hydrocarbons, whereas it is significantly larger in magnitude for parallel-displaced acenes. Moreover, there is a nonlinear increase in the interaction energy for the parallel-displaced acene dimers. Based on these considerations, Grimme concludes that stacked aromatics feature a "special" π-π interaction, not present in saturated hydrocarbons, which results from stabilizing electron correlation terms that only become significant when the two monomers are in close contact (leading to dispersion contributions which are more favorable than would be predicted by pairwise $-C_6R^{-6}$ terms). While our SAPT results and analysis support these conclusions, we note that the T-shaped configurations also feature a nonlinear increase in interaction energy, which is not present in the saturated hydrocarbons, all the way up to the largest dimer considered (pentacene dimer). Moreover, the dispersion energies for the T-shaped dimers are also larger than predicted by pairwise $-C_6R^{-6}$ terms. Hence, we see evidence in the T-shaped configurations, as well as the parallel-displaced configurations, of special π-π interactions. The dispersion terms in the T-shaped configurations are certainly smaller than in the parallel-displaced configurations, but they remain about 60% as large. The difference between the SAPT dispersion energy and the empirical $-C_6R^{-6}$ estimate remains about 40% as large. On this basis, even though the interaction energy of T-shaped acenes remains similar to that of stacked, saturated hydrocarbons of the same size, in our view special π-π interactions are also present in the T-shaped configurations, albeit to a lesser (but non-negligible) degree. This leads us to conclude that the close agreement between T-shaped acenes and stacked saturated dimers in plots of the interaction energy vs. dimer size (see Fig. 2 of Grimme's work[62]) is not an indication that the nature of the interactions is similar, but is an accident resulting from the very different geometries of those two sets of molecules. One could attempt to probe this hypothesis directly, by computing T-shaped saturated dimer energies, but unfortunately we could not come up with a reasonable chemical model that would fit this description without adding too many additional short-range contacts.

IV. CONCLUSIONS

We have applied the DF and CD approximations to wave function-based SAPT within a new program developed in the PSI 3.4 electronic structure package. Both DF and CD approaches have negligibly small errors compared to SAPT results using standard electron repulsion integrals. For our test cases, the auxiliary basis required for the 1C-CD approach is smaller than the corresponding DF basis. This could prove very useful for computations on large systems, where the expense associated with the formation of the three-index integrals is negligible compared to the formation of four-index MO integrals from three-index integrals.

We have applied our DF-SAPT code to the interactions within acene dimers. The new code is efficient enough that we were easily able to include the pentacene dimer in our tests. We determined the source of a discrepancy between SAPT and the EDA implementation previously used to study acene dimers by Grimme.[62] This difference was due to a problem with the EDA implementation. Both the T-shaped and the parallel-displaced configurations feature a nonlinear increase in interaction energy with respect to system size, all the way through pentacene dimer. Moreover, both types of configurations feature dispersion energies which are significantly larger than one would predict using pairwise $-C_6R^{-6}$ terms. Although these effects are smaller in magnitude for the T-shaped configurations due to the larger separation between the π-clouds, they do not become negligible. This suggests that special π-π interactions are present not only in parallel-displaced configurations, but also in T-shaped configurations of aromatic hydrocarbons.

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